

# Chemistry 163B Winter 2020

## notes for lecture 4- First Law Calculations

Chemistry 163B

Lecture 4

1<sup>st</sup> Law Calculations for Ideal Gases

Winter 2020

Challenged Penmanship

Notes

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*Menu: for TODAY(s)*

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- **Review of equivalent statements of 1<sup>st</sup> Law**
- **Ideal gas calculations for REVERSIBLE adiabatic expansion**  
*(fourth condition, viz lectures 2-3, slide #13)*
- **P, V, T constraints for reversible expansion ideal gas**  
*(HW#2 15)*
- **Cyclic path: combination of reversible adiabatic and isothermal expansions/compressions** *(HW#2 10, HELLO CARNOT CYCLE !!)*

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## notes for lecture 4- First Law Calculations

### 1<sup>st</sup> Law recapitulation

$U \equiv$  internal energy  
 $dU_{\text{sys}} = \delta q_{\text{sys}} + \delta w_{\text{sys}} + dn_{\text{sys}}$  (n=number of moles; dn=0 for closed system)  
 $dU_{\text{sys}} = -dU_{\text{surr}}$  (energy conserved)  
 $dU$  is exact differential  
 $U$  is a state function *completely general*

$$dU = \delta q + \delta w_{PV} + \delta w_{\text{other}} + dn$$

for only P-V work and closed system ( $\delta w_{\text{other}} = 0, dn=0$ )

$$dU = \delta q - P_{\text{ext}}dV$$

- Constant volume process  $dU_V = \delta q_V$      $\Delta U_V = q_V$
- Adiabatic process             $dU = \delta w$      $\Delta U = w$

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### isothermal expansion of ideal gas: concepts illustrated

10 atm  
300 K  
1 mole



1 atm  
300 K  
1 mole

	<b>irreversible</b> $P_{\text{ext}} = \text{const}$	<b>reversible</b> $P_{\text{ext}} = P_{\text{int}} = P$
isothermal expansion	$\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$	$\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$
<u><math>\Delta U</math></u>	<u>0</u>	<u>0</u>
<u><math>w = -\int P_{\text{ext}}dV</math></u>	$w = -P_{\text{ext}}(V_{\text{final}} - V_{\text{initial}})$ $= -nRT P_{\text{ext}} \left( \frac{1}{P_{\text{final}}} - \frac{1}{P_{\text{initial}}} \right)$ <u><math>= -2244 \text{ J}</math></u>	$w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$ $= +nRT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$ <u><math>= -5743 \text{ J}</math></u>
$q = -w$	<u><math>q = 2244 \text{ J}</math></u>	<u><math>q = 5743 \text{ J}</math></u>

- $\Delta U_{\text{irrev}} = \Delta U_{\text{rev}}$  ?? what can one say about the function U
- $\Delta V > 0, w < 0$  work is done ON ?? ON system or ON surroundings
- $q_{\text{irrev}} \neq q_{\text{rev}}$  ?? what does this imply about the quantities q and w and the differentials dq and dw
- $w_{\text{irrev}} \neq w_{\text{rev}}$  ?? which does more work ON surroundings rev or irrev

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### *two relationships for ideal gasses: a short look ahead* *(will prove rigorously in next lecture)*

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- for any substance (only P-V work)

$$dU_v = dq_v = n\bar{C}_v dT \quad \text{and} \quad \Delta U_v = \int n\bar{C}_v dT \quad \text{for a constant volume process}$$

- but for an ideal gas

$$dU = n\bar{C}_v dT \quad \text{and} \quad \Delta U = n\bar{C}_v \Delta T \quad \text{for ANY path (not only constant V process)}$$

*[other parts of path, i.e. changes of P and V with constant T, give zero contribution to  $\Delta U$ ]*

- for ideal gas

$$\bar{C}_p = \bar{C}_v + R$$

- monatomic ideal gas

$$\bar{C}_v = \frac{3}{2}R \quad \bar{C}_p = \frac{5}{2}R$$

*[simple proof coming soon]*

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### *adiabatic processes and the First Law*

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$$q = 0$$

$$\Delta U = w = -\int P_{ext} dV \quad \text{general}$$

$$\Delta U = n\bar{C}_v \Delta T \quad \text{ideal gas}$$

expansion  $\Delta V > 0$   $-\int PdV = w < 0$   $\Delta U < 0$  (ideal gas) system cools

compression  $\Delta V < 0$   $-\int PdV = w > 0$   $\Delta U > 0$  (ideal gas) system warms

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**Pressure-Volume work: irreversible adiabatic expansion  $P_{\text{ext}} = \text{constant}$**

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$P=10 \text{ atm}$

adiabatic  $q=0$

adiabatic

expansion

$P_{\text{ext}}=1 \text{ atm}$

**adiabatic expansion against constant pressure (irreversible)**

<p>1 mole 300K 10 atm <math>V_1</math></p>	<p><math>\Delta U = 0 + w = -P_{\text{ext}}(V_2 - V_1) = -1 \text{ atm} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)</math></p> <p><small>Will soon show holds for ideal gas V NOT const</small></p> <p><math>\Delta U = n\bar{C}_v \Delta T = \frac{3}{2} nR(T_2 - T_1)</math></p> <p><math>-1 \text{ atm} (1 \text{ mol}) R \left( \frac{T_2}{1 \text{ atm}} - \frac{300 \text{ K}}{10 \text{ atm}} \right) = \frac{3}{2} (1 \text{ mol}) R (T_2 - 300 \text{ K})</math></p>	<p>1 mole <math>T_2 ? \text{ K}</math> 1 atm <math>V_2</math></p>
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**brr!**  $T_2 = 192 \text{ K}$     $w = -1347 \text{ J} = -1.347 \text{ kJ}$    no q in, less work done than isothermal (-2.244 kJ)   **7**

**Pressure-Volume work reversible adiabatic expansion**

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$P=10 \text{ atm}$

adiabatic reversible

expansion

$P_{\text{ext}}=P_{\text{int}} (10 \text{ atm} \rightarrow 1 \text{ atm})$

- $q=0$
- $w = - \int P_{\text{ext}} dV$
- $\Delta U = q + w$
- $\Delta V > 0 \Rightarrow w < 0$  ( $w_{\text{surr}} > 0$ )
- $\Delta U = w < 0 \Rightarrow$  gas cools as  $V$  increases

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### *ideal gas adiabatic reversible processes WORK*

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$$w = - \int_{initial}^{final} P_{ext} dV \quad \text{work}$$

$$P_{ext} = P_{int} = P \quad \text{reversible}$$

$$P = \frac{nRT}{V} \quad \text{ideal gas}$$

so as before ??:

$$w = - \int_{initial}^{final} \frac{nRT}{V} dV \quad \text{DUH!}$$

~~$$w = -nRT \ln \frac{V_{final}}{V_{initial}}$$~~



but T varies along path initial → final

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### *for a reversible adiabatic expansion of ideal gas*

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important derivation (next few slides):

for reversible adiabatic expansion of ideal gas

want to relate (P,V,T) at any point along the reversible adiabatic path to

(P<sub>initial</sub>, V<sub>initial</sub>, T<sub>initial</sub>)

HW2 #15

STRATEGY:  $dU_{adiabatic} = \delta w = -PdV = n\bar{C}_V dT = dU_{ideal\ gas}$

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equating  $dU$  and work for reversible adiabatic process  $P_{\text{ext}}=P_{\text{int}}=P$

$$dU = \delta w = -PdV$$

$$dU = n\bar{C}_V dT = -PdV \quad (\text{ideal gas})$$

$$n\bar{C}_V dT = -\frac{nRT}{V} dV$$

$$\frac{\bar{C}_V}{R} \frac{dT}{T} = -\frac{dV}{V}$$

$$\int_{T_1=T_{\text{initial}}}^{T_2=T_{\text{final}}} \frac{\bar{C}_V}{R} \frac{dT}{T} = -\int_{V_1=V_{\text{initial}}}^{V_2=V_{\text{final}}} \frac{dV}{V}$$

$$\frac{\bar{C}_V}{R} \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = -\ln \frac{V_{\text{final}}}{V_{\text{initial}}} = \ln \frac{V_{\text{initial}}}{V_{\text{final}}}$$

or

$$\frac{\bar{C}_V}{R} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1} = \ln \frac{V_1}{V_2}$$

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for adiabatic, reversible, ideal gas:  $TvsV$

$$\left(\frac{T_2}{T_1}\right)^{\bar{C}_V/R} = \left(\frac{V_1}{V_2}\right)$$

$$\frac{\bar{C}_V}{R} \ln \frac{T_2}{T_1} = \ln \frac{V_1}{V_2}$$

$$\ln \left(\frac{T_2}{T_1}\right)^{\bar{C}_V/R} = \ln \frac{V_1}{V_2}$$

$$\left(\frac{T_2}{T_1}\right)^{\bar{C}_V/R} = \frac{V_1}{V_2}$$

$$T_2^{\bar{C}_V/R} V_2 = T_1^{\bar{C}_V/R} V_1$$

for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$   
along an adiabatic reversible path

know:  $T_{\text{initial}}, V_{\text{initial}}, V_{\text{final}} \rightarrow$  calculate  $T_{\text{final}}$   
 $T_{\text{initial}}, V_{\text{initial}}, T_{\text{final}} \rightarrow$  calculate  $V_{\text{final}}$

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*(other) T vs P relationship for adiabatic reversible (HW#15)*

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$$T_2^{\bar{C}_V} V_2 = T_1^{\bar{C}_V} V_1$$

with

$$\bar{C}_P = \bar{C}_V + R \quad \text{and} \quad V = \frac{nRT}{P}$$

$$T_2^{\bar{C}_V} V_2 = T_1^{\bar{C}_V} V_1$$

$$T_2^{\bar{C}_V} \frac{nRT_2}{P_2} = T_1^{\bar{C}_V} \frac{nRT_1}{P_1}$$

$$T_2^{\bar{C}_V+1} P_1 = T_1^{\bar{C}_V+1} P_2$$

$$T_2^{\bar{C}_V+R} P_1 = T_1^{\bar{C}_V+R} P_2$$

$$T_2^{\bar{C}_P} P_1 = T_1^{\bar{C}_P} P_2$$

$$\boxed{\frac{T_2^{\bar{C}_P}}{P_2} = \frac{T_1^{\bar{C}_P}}{P_1}}$$

for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$  along an adiabatic reversible path

know:  $T_{\text{initial}}, P_{\text{initial}}, P_{\text{final}} \rightarrow$  calculate  $T_{\text{final}}$  13

*summarizing (and HW2 #15)*

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$$\boxed{T_2^{\bar{C}_V} V_2 = T_1^{\bar{C}_V} V_1}$$

and

$$\boxed{\frac{T_2^{\bar{C}_P}}{P_2} = \frac{T_1^{\bar{C}_P}}{P_1}}$$

and

HW2 #15  $\rightarrow$   $\boxed{P_1 V_1^\gamma = P_2 V_2^\gamma}$  where  $\gamma = \frac{\bar{C}_P}{\bar{C}_V}$

**T vs V**

**T vs P**

**P vs V**

for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$  along an adiabatic reversible path

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adiabatic reversible expansion:  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$  what's  $T_f$ ??

EXAMPLE YEA !

$P_1=10 \text{ atm}$   
 $T_1=300\text{K}$   
 $V_1=2.462 \text{ l}$   
 $n=1 \text{ mol}$

$\longrightarrow$   $P_2=1 \text{ atm}$   
 $T_2=???$

use T vs P  $\frac{\bar{C}_p}{T_2^R} = \frac{\bar{C}_p}{T_1^R}$   
 $\frac{\bar{C}_p}{P_2} = \frac{\bar{C}_p}{P_1}$

$$\frac{\bar{C}_p}{T_2^R} = \frac{\bar{C}_p}{T_1^R} \quad \frac{\bar{C}_p}{R} = \frac{5}{2}$$

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{R}{\bar{C}_p}}$$

$$T_2 = T_1 \left( \frac{1 \text{ atm}}{10 \text{ atm}} \right)^{\frac{2}{5}} = 300\text{K} \times (0.1)^{\frac{2}{5}}$$

$T_2 = 300\text{K} \times (0.398) = 119.4\text{K}$

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adiabatic reversible expansion:  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$  what's  $V_f$ ??

ANOTHER EXAMPLE DOUBLE YEA ! YEA !!

$P_1=10 \text{ atm}$   
 $T_1=300\text{K}$   
 $V_1=2.462 \text{ l}$   
 $n=1$

$\longrightarrow$   $P_2=1 \text{ atm}$   
 $V_2=???$

use P vs V  $P_1V_1^\gamma = P_2V_2^\gamma$

$$P_2V_2^\gamma = P_1V_1^\gamma \quad \gamma = \frac{\bar{C}_p}{\bar{C}_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$V_2 = V_1 \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} = V_1 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}}$$

$$V_2 = V_1 \left( \frac{10 \text{ atm}}{1 \text{ atm}} \right)^{\frac{3}{5}} = 2.46\text{l} \times (10)^{\frac{3}{5}}$$

$V_2 = 2.462\text{l} \times (3.98) = 9.80\text{l}$

also:

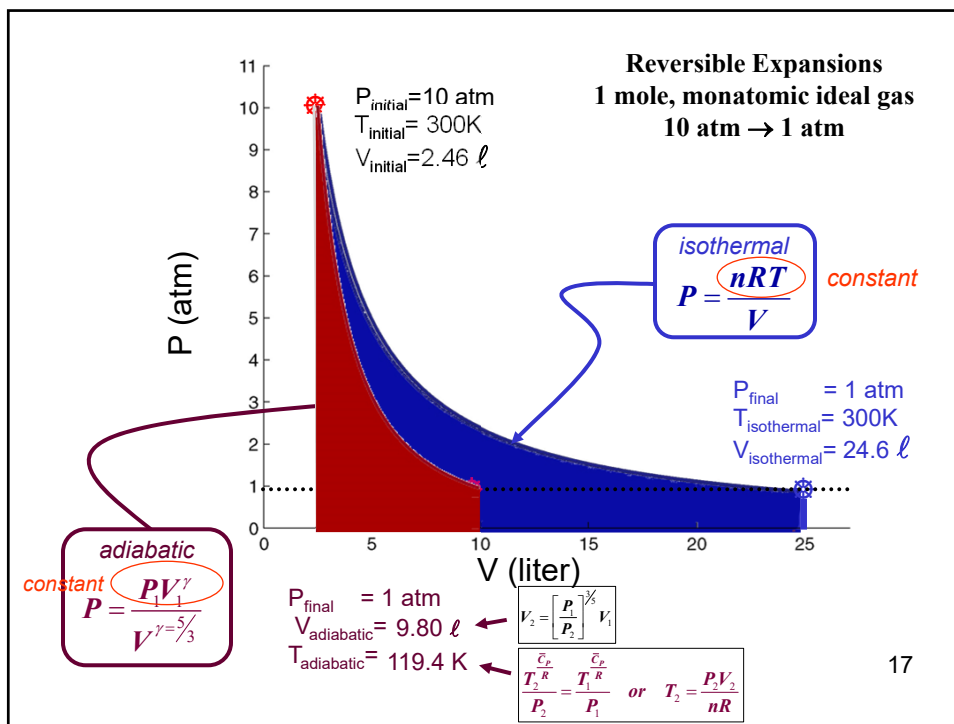
$V_2 = \frac{nRT_2}{P_2}$   
 $V_2 = \frac{1\text{mol}(.0821 \text{ l atm mol}^{-1}\text{K}^{-1})(119.4\text{K})}{1 \text{ atm}}$   
 $V_2 = 9.80 \text{ l}$

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adiabatic reversible expansion:  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$

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calc  $\Delta U$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = (119.4 - 300) \text{ K} = -180.6 \text{ K}$$

$$\Delta U = n \bar{C}_V \Delta T = (1 \text{ mol}) (1.5) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (-180.6 \text{ K})$$

$$\Delta U = -2.257 \text{ kJ}$$

calc  $q, w$

$q = 0$

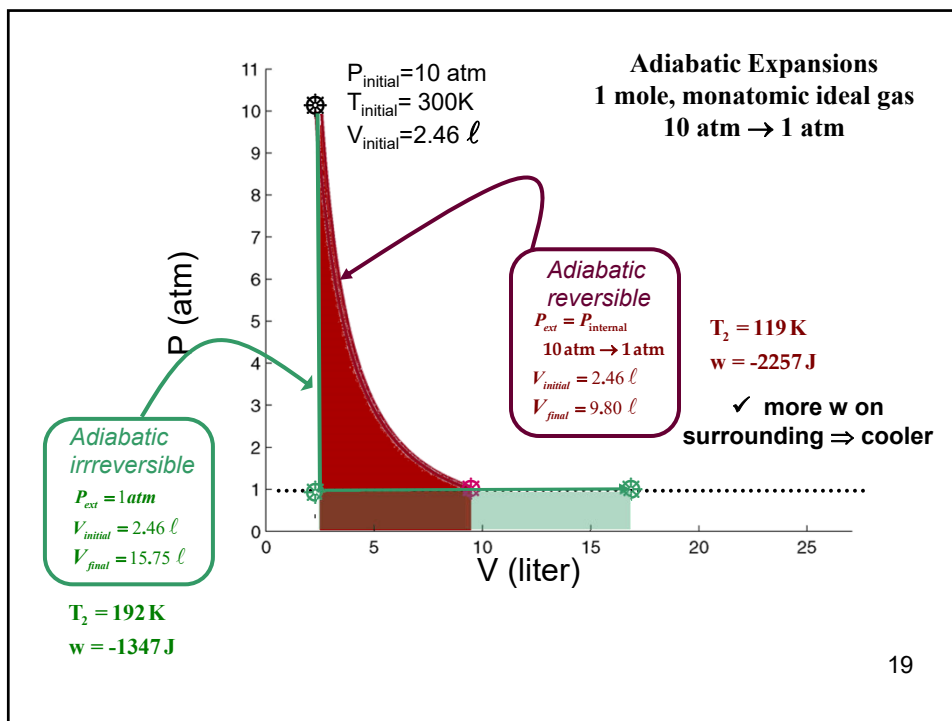
$$q + w = \Delta U \Rightarrow w = -2.257 \text{ kJ}$$

vs -5.743 kJ for isothermal reversible  
10 atm → 1 atm at 300K

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### HW#2 Problem 10 (Raff 2.14)

10. [from Raff #2.14] One mole of an ideal gas at a temperature of 500 K and a pressure of 6 atm is subjected to the following changes:

**STEP 1:** The gas is expanded isothermally and reversibly to a final pressure of 5 atm.

**STEP 2:** After completion of STEP 1, the gas is expanded adiabatically and reversibly until the pressure reaches 4 atm.

**STEP 3:** After STEP 2 is completed, the gas is compressed isothermally and reversibly to a final pressure of 4.800 atm.

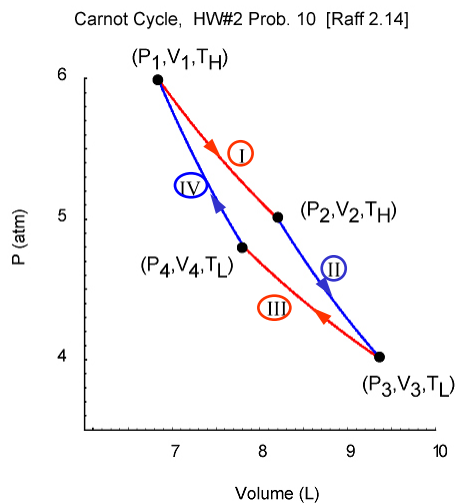
**STEP 4:** After STEP 3, the gas is compressed adiabatically and reversibly to a pressure of 6 atm, returning the gas to a temperature of 500 K.

- a. Compute  $w$ ,  $q$ , and  $\Delta U$  for STEP 1.
- b. At the completion of STEP 2, what are the temperature and volume of the gas? Compute the amount of work done in STEP 2.
- c. Compute  $w$ ,  $q$ , and  $\Delta U$  for STEP 3.
- d. Compute the amount of work done in STEP 4.
- e. Compute  $w$ ,  $q$ , and  $\Delta U$  for the entire process.

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### Problem HW#2 Prob10



#### cyclic process

- I isothermal expansion
- II adiabatic expansion
- III isothermal compression
- IV adiabatic compression

$$P_1 = 6 \text{ atm}, T_1 = T_H = 500 \text{ K}$$

$$P_2 = 5 \text{ atm}, T_2 = T_H = 500 \text{ K}$$

$$P_3 = 4 \text{ atm}, q_{2 \rightarrow 3} = 0, T_3 = T_L$$

$$P_4 = 4.8 \text{ atm}, T_4 = T_L, q_{4 \rightarrow 1} = 0$$

HINT:  $T_L = 457.3 \text{ K}$

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You've Made IT



## Ideal Gas Calculations and the First Law 'four paths to enlightenment'

handout # 10 provides a summary of  
our work on calculations and  
interpretations for ideal gas  
expansions and compressions

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## notes for lecture 4- First Law Calculations

Menu: for TODAY(s)

**DONE !!**



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- ✓ **Review of equivalent statements of 1<sup>st</sup> Law**
- ✓ **Ideal gas calculations for REVERSIBLE adiabatic expansion**  
*(fourth condition, viz lectures 2-3, slide #13)*
- ✓ **P, V, T constraints for reversible expansion ideal gas**  
*(HW#2 15)*
- ✓ **Cyclic path: combination of reversible adiabatic and isothermal expansions/compressions** *(HW#2 10, HELLO CARNOT CYCLE !!)*

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End of Lecture 4

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